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Novel Pyridinium Surfactants with Unsaturated Alkyl Chains: Aggregation Behavior and Interactions with Methyl Orange in Aqueous Solution

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This paper presents the synthesis and a study of the aggregation behavior of 4-undecyl-1-methyl- and 4-undecenyl-1-methylpyridinium iodide surfactants. The effect of the position of the double bond in the alkyl chain of the surfactant on the critical micelle concentration (cmc), degree of counterion binding (β), Krafft temperature, and thermodynamic parameters of micelle formation has been investigated. Also, a pyridinium surfactant with a triple bond in the alkyl chain has been studied. The cmc values of the surfactants increase after the introduction of a double bond or a triple bond in the tail as compared to the saturated equivalents. The largest effect was observed for surfactants with a cis-oriented double bond in the alkyl chain. The enthalpies of micelle formation ($\Delta H°$) were shown to be exothermic. Introduction of an unsaturation in the tail leads to an increase of the enthalpy of micelle formation. The largest effect is observed for 4-(1-undecynyl)-1-methylpyridinium iodide. The influence of a double bond in the tail of the surfactants on the absorption spectrum of methyl orange (MO) complexed to the surfactant was studied by UV−vis spectroscopy. Low concentrations of 4-alkyl-1-alkylpyridinium amphiphiles induce a new, ca. 80-nm, blue-shifted band. However, the surfactants 4-(10-undecenyl)-1-methylpyridinium iodide, 4-(5-*cis*-undecenyl)-1-methylpyridinium iodide, and 4-(5-*trans*-undecenyl)-1-methylpyridinium iodide do not induce this absorption band at short wavelengths. In contrast, 4-(1-undecenyl)-1-methylpyridinium iodide and 4-(1-undecynyl)-1-methylpyridinium iodide showed this short wavelength absorption band positioned at 383 nm.

Introduction

The influence of a double bond in the hydrocarbon tail of surfactant molecules on the aggregation behavior has been studied.[1−7] Introduction of a double bond generally causes a small but definite increase in the observed critical micelle concentration (cmc) values. Sodium oleate (C_{18}, cis double bond at C_9) shows a 3× higher cmc as compared to the saturated compound, whereas sodium elaidate (C_{18}, trans double bond at C_9) shows an even larger cmc increase.[1] Terminally unsaturated sodium carboxylates increase the cmc by a factor of 2 with respect to the corresponding saturated compounds.[2−4] Recently, sodium carboxylates with a double bond located near the headgroup have also been studied.[5] It was found that the cmc values increase as the number of double bonds increases. Damas et al.[6] studied the influence of structural modifications near the ionic headgroup of sodium carboxylates on their aqueous solution behavior. No appreciable effect on the cmc due to cis/trans isomerism of the double bond was noticed. The effect of unsaturation on the overall length of the alkyl chain in comparison with saturated surfactant corresponds to a decrease of the straight alkyl chain length by only 1/10 of a CH_2 group. Yokoyama et al.[7] showed that the cmc values of eicosapolyenic acids (C_{20} sodium alkanoate, double bonds at several positions) increase approximately 2-fold by every additional double bond. Moreover, the effect of a double bond on the cmc depends primarily on the number of unsaturations rather than on their position within the chain.

Most of these studies deal, however, with anionic surfactants. In the present study, cationic surfactants were investigated. The effects of structural variations in cationic pyridinium surfactants have been widely studied in our group.[8−12] These include variation of the tail length, branching of the tail, variation of the alkyl group attached to the pyridine nitrogen atom, and variation of the counterion. The change in the logarithm of the cmc as a function of the tail length for surfactants with linear alkyl chains has been described by the Shinoda equation,[13] yielding a linear correlation.[9] An increase in the length of the alkyl group on the nitrogen of the pyridine leads to a lower cmc value due to the increasing hydrophobicity of the surfactant.[8] For chain lengths of four carbons or more, vesicles are formed. When the counterion is changed from iodide to bromide to chloride, the cmc also has a

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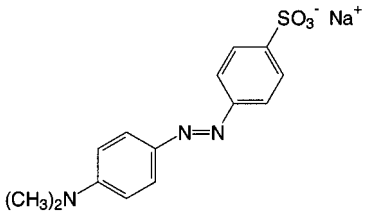

Figure 1. Structure of MO.

tendency to increase,[11,14] whereas branching of the alkyl chain leads to higher cmc values as compared to the linear analogues with the same number of carbons in the chain.[12]

In the present study, cationic pyridinium surfactants with an unsaturation at different positions in the tail were synthesized, and their aggregation behavior has been studied. The cmc values of the surfactants were determined using conductivity and microcalorimetry. The latter technique also provided the thermodynamic parameters of micelle formation. The influence of a double bond in the hydrocarbon tail of surfactants on the packing in the micelle has also been studied by NMR relaxation methods. NMR T_1 relaxation studies in the presence of paramagnetic additives were used to localize solubilizates[15,16] and to determine distribution coefficients for solubilizates in micelles.[17,18] The conformational behavior of hydrocarbon tails of surfactants in micelles was also studied by NMR relaxation studies with added aliquots of paramagnetic ions.[19] In most papers, the ^{13}C T_1 relaxation times were measured. The spin−lattice relaxation rate is dramatically enhanced close to paramagnetic ions and, moreover, shown to be highly distance dependent. The paramagnetic ions are located at the surface of the micelles and therefore in close proximity to the surface-oriented nuclei of the surfactant. These will therefore experience the influence of the paramagnetic ion more strongly than nuclei in the inner core of the micelle. In this study, the packing of the surfactants in the micelle is studied by ^1H T_1 relaxation measurements due to limited solubility and low concentrations, excluding the application of ^{13}C NMR techniques.

The influence of surfactants on the absorption spectrum of dyes has been a subject of research since the last century. Especially, the short wavelength absorption band, as induced by low concentrations of surfactant, has been investigated extensively. Methyl Orange (MO, Figure 1) is an example of an anionic azo dye showing interactions with several cationic surfactants.

The wavelength of maximum absorption establishes a blue shift after addition of small amounts of cationic surfactants.[20−25] The origin of this band is still under debate, although several explanations (including cis/trans isomerism[22,26] and ion-pair formation)[23] have evolved over the years. An interesting and most likely explanation involves the formation of dye aggregates in parallel orientations, so-called H-aggregates.[20,24,27] Interaction between the transition dipoles causes a splitting of the monomer excited state. When an H-aggregate (parallel orientation of the dipole moments) is formed, a blue shift is predicted. In cast films of an azobenzene-containing amphiphile, a parallel orientation of azobenzene units has been confirmed by X-ray diffraction experiments.[28] Buwalda et al.[24] have investigated the influence of the alkyl chain length of alkyltrimethylammonium bromides and of *N*-methyl-4-alkylpyridinium iodides on the absorption spectrum of several azo dyes. For the shorter chains, higher concentrations of the dye were needed in order to induce aggregation. Because the aggregation behavior of surfactants is influenced by unsaturation(s), a study toward the influence of the position of the double bond in the alkyl chain of surfactants appeared challenging.

Experimental Section

Materials. MO, 9-decen-1-ol, *cis*-4-decenal, 1-bromodecane, and 4-bromopyridine hydrochloride were purchased from Acros Organics, whereas *trans*-4-decenal was obtained from Fluka. MO was crystallized from doubly distilled water. Water was demineralized and distilled twice in an all-quartz distillation unit. 4-(Undecane)-1-methylpyridinium iodide was synthesized according to a literature procedure.[9] Melting points (uncorrected) were determined using a Kofler hot stage.

NMR Measurements. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Varian VXR-300 spectrometer operating at 300 MHz for ^1H, on a Varian Gemini-200 spectrometer operating at 50 MHz for ^{13}C, and on a Varian UnityPlus 500 MHz spectrometer operating at 125 MHz for ^{13}C. The residual ^1H signal of the deuterated solvents was used as an internal chemical shift standard. T_1 relaxation measurements were performed on a Varian UnityPlus 500 MHz spectrometer using an inversed recovery pulse sequence. All data processing was performed using standard Varian VnmrS/VnmrX software packages. The solutions contained 0 or 0.4 mM $[Cu(EDTA)]^{2-}$ and 50 mM surfactant. Concentrations between 0 and 1.4 mM were used for the measurement in which the $[Cu(EDTA)]^{2-}$ concentration was varied.

UV−Vis Spectroscopy. UV−vis adsorption spectra were recorded using a Perkin-Elmer λ-2, λ-5, or λ-12 spectrophotometer equipped with thermostated cell compartments. The concentration of MO used throughout this study was 25 μM, and the cell was thermostated at 25 °C.

Conductivity Experiments. The conductivity method was used to determine the cmc and the degree of counterion binding. The measurements were carried out on a Wayne-Kerr Autobalance Bridge B642 equipped with a Philips electrode PW 951201. Solutions in the conductivity cell were stirred magnetically and thermostated at 25 °C. Surfactant concentrations were varied by the addition of 25−100 μL portions of a concentrated stock solution of surfactant to the conductivity measuring cell. Concentrations were corrected for volume changes.

Differential Scanning Calorimetry (DSC). DSC experiments were performed using a Perkin-Elmer DSC-7 apparatus in stainless steel pans. The reference cell contained an empty pan. Heating and cooling scans were run in triple with scan rates of 3 deg min^{-1}. The concentration of **5** was 170 mM.

Microcalorimetry. An Omega isothermal titration microcalorimeter was used to measure the enthalpies of micelle formation. The experiments were performed at 25 °C. A sequence of 30 injections of 10 μL of an aqueous surfactant solution with a concentration of 20× the cmc, typically, was added with a

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syringe into the sample cell containing 1.4 mL of pure water at the start of the experiment. For each injection, an endothermic peak was observed. The solution was stirred at 6 Hz. The time between two injections was 210 s.

Synthesis of 4-Decenol (7a,b). The synthesis of *cis*-4-decenol (**7b**)[29] is described as an example. Similar conditions were used for the preparation of **7a**.[30]

***cis*-4-Decenol (7b).** To 0.6 g (15.8 mmol) of $LiAlH_4$ in 100 mL of dry diethyl ether was added dropwise a solution of 3.11 g (20.2 mmol) of *cis*-4-decenal in 20 mL of diethyl ether. The mixture was stirred for 90 min. Subsequently, the mixture was cooled to 0 °C, and sulfuric acid (10%) was slowly added until the excess of $LiAlH_4$ was deactivated. The organic layer was washed with 100 mL of water. The resulting aqueous layer was extracted with 25 mL of diethyl ether. Finally, the combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting colorless liquid was purified by bulb to bulb distillation, yielding 64% of *cis*-4-decenol. The spectroscopic data were shown to be in agreement with literature values.[29] *trans*-4-Decenol (**7a**) was obtained in 81% overall yield.

Syntheses of 1-Bromo-*x*-decene (8a−c) (*x* = 4, 10). The synthesis of 1-bromo-10-decene (**8c**)[31] is described as an example. Similar conditions were used for the preparation of **8a**[32] and **8b**.[33]

1-Bromo-10-decene (8c). To a solution of 5.09 g (33 mmol) of 9-decen-1-ol in 50 mL of dry diethyl ether was added 100 μL of pyridine under a nitrogen atmosphere. Subsequently, the reaction mixture was cooled to approximately 0 °C, and 1.20 mL of PBr_3 (13 mmol) in 50 mL of dry diethyl ether was added dropwise. The mixture was stirred overnight at room temperature. Hereafter, the mixture was refluxed for 2 h; after being cooled, 100 mL of a saturated aqueous solution of $NaHCO_3$ was added slowly; and the layers were separated. The ether layer was washed with 100 mL of water, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting colorless liquid was chromatographed over silica gel with hexane/ethyl acetate (10/1) as an eluent, yielding 1-bromo-10-decene (54%) as a colorless liquid. The spectroscopic data were shown to be in agreement with literature values.[31] **8a** was obtained in 62% yield, and **8b** was obtained in 50% yield.

Syntheses of 4-(*x*-Undecenyl)pyridine (9a−c) (*x* = 5, 10). The synthesis of 4-(10-undecenyl)pyridine (**9c**) is described as an example. Similar conditions were used for the preparation of **9a** and **9b**.

4-(10-Undecenyl)pyridine (9c). To a stirred solution of 0.96 mL (6.8 mmol) of diisopropylamine in 100 mL of dry diethyl ether was added 4.3 mL of *n*-butyllithium (6.8 mmol, 1.6 M in hexane) under a nitrogen atmosphere and stirred for 15 min. The mixture was cooled to −20 °C, and 0.67 mL (6.8 mmol) of 4-methylpyridine was added. The mixture was stirred for 30 min at −20 °C. Subsequently, 1.5 g (6.8 mmol) of 1-bromo-10-decene in 50 mL of diethyl ether was added dropwise. The mixture was allowed to react at −20 °C for 60 min and overnight at room temperature. After addition of 100 mL of water and separation of the two layers, the aqueous layer was extracted with 75 mL of diethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting slightly yellowish oil was chromatographed over Al_2O_3 (act. II−III, neutral) using ether/hexane (50/50) as an eluent. 4-(10-Undecenyl)pyridine (**9c**) was obtained as a slightly yellowish oil in 59% yield. The yields of **9a**,**b** were 36 and 65%, respectively.

4-(5-*trans*-Undecenyl)pyridine (9a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, J = 6.8 Hz, 3H), 1.21−1.41 (m, 8H), 1.60 (m, 2H), 1.91−2.02 (m, 4H), 2.58 (t, J = 7.6 Hz, 2H), 5.28−5.38 (m, 2H), 7.08 (d, J = 5.9 Hz, 2H), 8.45 (d, J = 5.9 Hz, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1, 22.5, 29.0, 29.3, 29.7, 31.4, 32.2, 32.5, 35.1, 124.0, 129.6, 131.0, 149.3, 152.0.

4-(5-*cis*-Undecenyl)pyridine (9b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (t, J = 7.0 Hz, 3H), 1.27−1.43 (m, 8H), 1.64 (m, 2H), 1.95−2.08 (m, 4H), 2.63 (t, J = 7.7 Hz, 2H), 5.28−5.39 (m, 2H), 7.16 (d, J = 5.9 Hz, 2H), 8.47 (d, J = 5.9 Hz, 2H). ^{13}C NMR (500 MHz, $CDCl_3$): δ 14.1, 22.5, 26.8, 27.1, 29.1, 29.3, 29.7, 31.4, 35.1, 124.1, 128.9, 130.4, 148.6, 152.7.

4-(10-Undecenyl)pyridine (9c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, J = 6.6 Hz, 3H), 1.20−1.24 (m, 16H), 1.53−1.60 (m, 2H), 2.58 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 4.7 Hz, 2H), 8.44 (d, J = 6.2 Hz, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 28.9, 29.0, 29.0, 29.3, 29.3, 30.2, 33.7, 35.1, 114.0, 123.7, 139.0, 149.5, 151.6.

4-(1-Undecynyl)pyridine (10). A solution of 2.55 g of 4-bromopyridine hydrochloride (13.1 mmol), 125 mg of bis-(triphenylphosphine)palladium(II) chloride (0.18 mmol), 3.0 mL of undecyne (15.2 mmol), and 123 mg of CuI (0.65 mmol) in 15 mL of diethylamine was stirred at room temperature for 18 h. Diethyl ether (25 mL) was added, and the solution was washed with 30 mL of water. The aqueous layer was washed with 25 mL of diethyl ether. Finally, the combined ether layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The black sticky oil was purified by bulb to bulb distillation (120 °C, 0.2 mbar) and additionally by chromatography over Al_2O_3 (act. II−III, neutral) using ether/hexane (50/50) as the eluent. 4-(1-Undecynyl)pyridine was obtained as a slightly yellowish oil in 64% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.82 (t, J = 6.6 Hz, 3H), 1.21−1.23 (m, 10H), 1.35−1.39 (m, 2H), 1.50−1.59 (m, 2H), 2.33 (t, J = 6.9 Hz, 2H), 7.18 (d, J = 5.85 Hz, 2H), 8.46 (d, J = 4.4 Hz, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.4, 19.4, 22.6, 28.3, 28.9, 29.1, 29.2, 29.4, 31.8, 78.4, 96.1, 125.8, 132.3, 149.5.

4-(1-*trans*-Undecenyl)pyridine (11). To 11 mL of a solution of $LiAlH_4$ in tetrahydrofuran (THF, 11 mmol, 1 M) was added 979 mg of 4-(1-undecynyl)pyridine (4.27 mmol). The mixture was stirred overnight at room temperature. The reaction mixture was quenched with a few drops of water. Diethyl ether (25 mL) was added, and the solution was washed with 30 mL of water. The resulting aqueous layer was washed with 25 mL of diethyl ether. The combined ether layers were dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure. The resulting oil was chromatographed over Al_2O_3 (act. II−III, neutral) using ether/hexane (50/50) as the eluent. 4-(1-*trans*-Undecenyl)pyridine was obtained in 47% yield. (95% trans and 5% cis as shown by NMR.)

^{1}H NMR (300 MHz, CD_3OD): δ 0.82 (t, J = 6.6 Hz, 3H), 1.22−1.26 (m, 12H), 1.39−1.46 (m, 2H), 1.41−1.46 (m, 2H), 2.19 (q, J = 6.8 Hz, 2H), 6.33 (d, J = 15.7 Hz, 1H), 6.52−6.62 (m, 1H), 7.31 (d, J = 6.22 Hz, 2H), 8.32 (d, J = 6.22 Hz, 2H). ^{13}C NMR (500 MHz, CD_3OD): δ 14.5, 23.7, 30.0, 30.4, 30.5, 30.6, 30.7, 33.1, 34.1, 122.3, 128.7, 138.6, 147.9, 150.1.

4-(*x*-Undecenyl)-1-methylpyridinium Iodide (2−5) (*x* = 1, 5, 10) and 4-(1-Undecynyl)-1-methylpyridinium Iodide (6). The synthesis of 4-(1-undecenyl)-1-methylpyridinium iodide (**5**) is described as an example. Similar conditions were used for the preparation of **2**−**4** and **6**.

4-(1-Undecenyl)-1-methylpyridinium Iodide (5). To a stirred solution of 0.20 g (0.86 mmol) of 4-(1-*trans*-undecenyl)-pyridine in 2 mL of acetone was added 0.5 mL of methyl iodide. The mixture was stirred overnight at room temperature. The solvent was removed by evaporation under reduced pressure. Surfactant **5** was obtained as a yellow crystalline solid in 95% yield, whereas surfactant **3** was obtained as a yellow/brown wax. Surfactants **2**−**4** and **6** were synthesized in a similar way with yields between 71 and 95%, respectively.

4-(10-Undecenyl)-1-methylpyridinium Iodide (2). mp 93−96 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18−1.38 (m, 12H), 1.62−1.76 (m, 2H), 2.02 (q, 2H), 2.86 (t, 2H), 4.63 (s, 3H), 4.86−5.02 (m, 2H), 5.68−5.89 (m, 1H), 7.80 (d, 2H), 9.10 (d, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 28.6, 28.8, 28.9, 29.0, 29.1, 29.1, 29.4, 33.5, 35.7, 48.2, 113.9, 127.7, 138.9, 144.5, 163.2. Anal. Calcd for $C_{17}H_{28}NI$ (373.32): C, 54.70; H, 7.50; N, 3.80. Found: C, 54.57; H, 7.51; N, 3.70.

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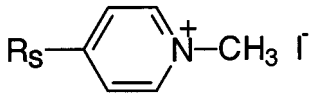
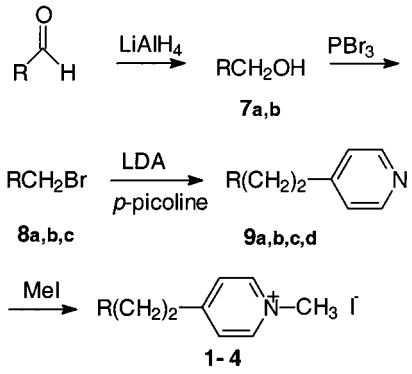


Figure 2. Structures of the surfactants used in this study. R_S: **1**, $CH_3(CH_2)_{10}$; **2**, $CH_2{=}CH(CH_2)_9$; **3**, *cis*-$CH_3(CH_2)_4CH{=}CH(CH_2)_4$; **4**, *trans*-$CH_3(CH_2)_4CH{=}CH(CH_2)_4$; **5**, $CH_3(CH_2)_8CH{=}CH$; and **6**, $CH_3(CH_2)_8CH{\equiv}CH$.

Scheme 1. Synthesis of Surfactants 1−4[a]



[a] Key (R): **a**, *trans*-$CH_3(CH_2)_4CH{=}CH(CH_2)_2$; **b**, *cis*-$CH_3(CH_2)_4CH{=}CH(CH_2)_2$; **c**, $CH_2{=}CH(CH_2)_7$; and **d**, $CH_3(CH_2)_8$.

4-(5-*cis*-Undecenyl)-1-methylpyridinium Iodide (3). Waxy solid; ^{1}H NMR (300 MHz, CD_3OD): δ 0.84 (t, J = 7.0 Hz, 3H), 1.24−1.31 (m, 6H), 1.41 (q, J = 7.5, 2H), 1.71 (qt, 2H), 1.95−2.09 (m, 4H), 2.90 (t, J = 7.7 Hz, 2H), 4.31 (s, 3H), 5.29−5.33 (m, 2H), 7.89 (d, J = 6.6 Hz, 2H), 8.71 (d, J = 6.6, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.0, 22.5, 26.6, 27.2, 29.1, 29.3, 31.4, 35.8, 48.8, 127.8, 128.4, 131.0, 145.0, 163.0. Anal. Calcd for $C_{17}H_{28}NI$ (373.32): C, 54.69; H, 7.56; N, 3.75. Found: C, 54.41; H, 7.56; N, 3.62.

4-(5-*trans*-Undecenyl)-1-methylpyridinium Iodide (4). mp 90−91 °C dec; ^{1}H NMR (300 MHz, CD_3OD): δ 0.80 (t, J = 6.8 Hz, 3H), 1.16−1.31 (m, 6H), 1.32−1.42 (m, 2H), 1.61−1.72 (m, 2H), 1.86−1.92 (m, 2H), 1.94−2.01 (m, 2H), 2.86 (t, J = 7.7 Hz, 2H), 4.26 (s, 3H), 5.27−5.38 (m, 2H), 7.84 (d, J = 6.2 Hz, 2H), 8.65 (d, J = 6.6 Hz, 2H). ^{13}C NMR (200 MHz, CD_3OD): δ 14.4, 23.6, 30.1, 30.3, 30.4, 32.5, 33.2, 33.6, 36.4, 48.3, 128.9, 130.7, 132.2, 146.0, 164.7. Anal. Calcd for $C_{17}H_{28}NI$ (373.32): C, 54.69; H, 7.56; N, 3.75. Found: C, 53.99; H, 7.42; N, 3.74.

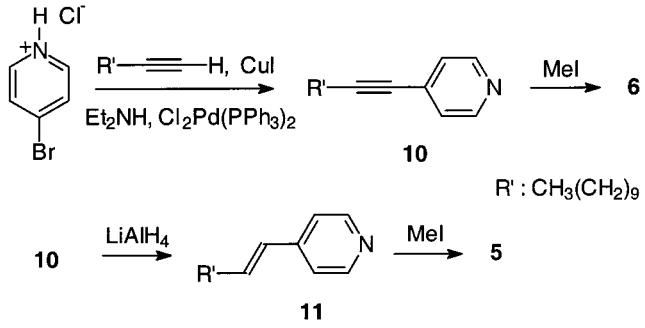
4-(1-Undecenyl)-1-methylpyridinium Iodide (5). Surfactant **5** shows a complex melting behavior; therefore, a melting point is not given. ^{1}H NMR (300 MHz, CD_3OD): δ 0.89 (t, J = 6.6 Hz, 3H), 1.30−1.35 (m, 12H), 1.52−1.59 (m, 2H), 2.39 (q, J = 6.8 Hz, 2H), 4.30 (s, 3H), 6.68 (d, J = 15.7 Hz, 1H), 7.11−7.21 (m, 1H), 8.00 (d, J = 6.9 Hz, 2H), 8.69 (d, J = 6.6 Hz, 2H). ^{13}C NMR (200 MHz, CD_3OD): δ 14.4, 23.7, 29.5, 30.4, 30.4, 30.5, 30.6, 33.0, 34.6, 47.9, 124.8, 126.7, 146.2, 148.1, 155.3. Anal. Calcd for $C_{17}H_{28}NI$ (373.32): C, 54.70; H, 7.56; N, 3.75. Found: C, 54.80; H, 7.38; N, 3.84.

4-(1-Undecynyl)-1-methylpyridinium Iodide (6). mp 117−118 °C dec; ^{1}H NMR (300 MHz, CD_3OD): δ 0.89 (t, J = 6.6 Hz, 3H), 1.30−1.32 (m, 10H), 1.43−1.50 (m, 2H), 1.62−1.72 (m, 2H), 2.60 (t, J = 7.1 Hz, 2H), 7.95 (d, J = 6.6 Hz, 2H), 8.80 (d, J = 6.6 Hz, 2H). ^{13}C NMR (200 MHz, CD_3OD): δ 12.4, 18.5, 21.9, 27.0, 28.0, 28.2, 28.4, 28.6, 31.0, 46.7, 75.5, 106.9, 128.8, 144.4. Anal. Calcd for $C_{17}H_{26}NI$ (371.30): C, 54.99; H, 7.05; N, 3.77. Found: C, 55.00; H, 7.03; N, 3.77.

Results and Discussion

Synthesis. Structural formulas of the surfactants are shown in Figure 2. The starting aldehydes were reduced to the corresponding alcohols using $LiAlH_4$ in THF[34] (Scheme 1). The alcohols were subsequently brominated using PBr_3 in diethyl ether.[35] Pyridines **9a**−**d** were prepared starting from *p*-picoline, the appropriate alkyl bromide and lithium diisopropylamide, using the general method as described by Sudhölter.[36] Finally, the pyridine was N-methylated using MeI in acetone.

Scheme 2. Synthesis of Surfactants 5 and 6



The synthesis of surfactants **5** and **6**, which possess an unsaturation directly adjacent to the headgroup, is depicted in Scheme 2. Pyridine **10** was prepared starting from the HCl salt of 4-bromopyridine and undecyne. The reaction was carried out in diethylamine using CuI and $(PPh_3)_2PdCl_2$ as catalysts.[37] It has to be noted that the reaction should be performed in a concentrated solution as described in the Experimental Section; otherwise, the reaction proceeds unacceptably slow. The triple bond of pyridine **10** was reduced with $LiAlH_4$ in THF to pyridine **11** with a trans-oriented double bond. To prepare the cis alkene, the triple bond of pyridine **10** was reduced with H_2 and Pd on $CaCO_3$ as the catalyst.[38] In addition to the *cis*-alkenylpyridine, the *trans*-alkenylpyridine and the alkylpyridine were also formed in up to 15% yield. Isolation of the *cis*-alkenylpyridine by chromatography and subsequent methylation of the pyridine nitrogen yielded *cis*-alkenylpyridinium surfactant. However, the obtained surfactant isomerized under the reaction conditions to a ratio of 60% cis and 40% trans as determined by ^{1}H NMR.

cmc Measurements. The cmc values of surfactants **1**−**4** and **6** were determined by conductometry and microcalorimetry. The latter method also provided the thermodynamic parameters of micelle formation. The cmc of surfactant **5** could not be determined due to its Krafft temperature of 57.1 °C as determined by DSC. Both the microcalorimeter and the conductometer were not equipped to perform measurements at this temperature.

The cmc values were determined from plots of the conductivity against the surfactant concentration. A typical plot is shown in Figure 3. A clear break at the cmc was observed for all the surfactants. The results of the measurements are summarized in Table 1.

The introduction of a double bond in the tail of the surfactant has several implications. First, the tail becomes shorter as a double bond is slightly shorter as compared to a single bond. Second, a double bond is less hydrophobic than a single bond. The hydrophobic fragmental constant (Σf) for a $CH_2{-}CH_2$ group is 1.476, and for a $CH{=}CH$ group, it is 0.63, a significant difference.[39] The third effect is hampering of the packing of the tails in the core of the micelle for the less flexible unsaturated tails. These effects lead to an increase in the cmc as compared to the corresponding saturated compound. Factors that determine the cmc (among other factors) are the hydrophobicity

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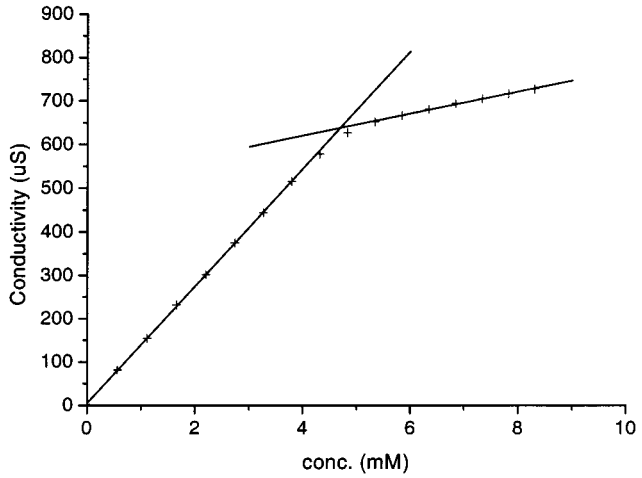

Figure 3. Typical plot of conductivity vs concentration for **1** at 25 °C.

Table 1. cmc Values (Determined by Conductivity and Microcalorimetry), Degrees of Counterion Binding (β), and Changes in Effective Chain Length (Δn) of 1−4 and 6

surfactant	cmc (mM)[a]	cmc (mM)[b]	β[a]	Δn
1	4.7	5.2	0.82	
2	9.3	10.7	0.77	−0.8
3	11.6	12.9	0.78	−1.2
4	9.2	10.5	0.80	−0.8
6	7.9	8.9	0.82	−0.6

[a] From conductivity measurements. [b] From microcalorimetric measurements.

of the monomers in water and the ease of alkyl chain packing in micelles.

As anticipated, surfactant **1** has the lowest cmc. Surfactant **3** has a higher cmc than surfactant **4** with the trans double bond. This was not expected on the basis of the results from Klevens,[1] which showed that the sodium alkanoate with the trans double bond has a higher cmc than the alkanoate with the cis-configured double bond. However, a cis double bond is expected to hamper the chain packing more than a trans double bond, so the higher cmc found for surfactant **3** is reasonable. Because surfactants **2** and **4** have comparable cmc values, it can be concluded that the Gibbs energy of micelle formation is comparable. The triple bond adjacent to the headgroup has a smaller effect on the cmc than a double bond at other positions in the tail. Nusselder et al.[9] found a cmc value of 13 mM (25 °C) for 1-methyl-4-(5-dodecynyl)-pyridinium iodide and 2.50 mM (30 °C) for the corresponding saturated compound. In comparison with our results, it is obvious that a triple bond in the middle of the alkyl tail increases the cmc more than a triple bond adjacent to the headgroup.

The cmc values as determined by microcalorimetry are slightly higher than the cmc values as determined by conductometry. Relatively minor differences in cmc values as obtained by different methods are, however, commonly observed.[40]

The approximate degree of counterion binding (β) was calculated by the following equation:

$$\beta = 1 - \frac{dk/dC_{\text{before cmc}}}{dk/dC_{\text{after cmc}}} \qquad (1)$$

in which k is the conductivity and C is the surfactant concentration. The obtained β values are generally common for these types of surfactants. 1-Methyl-4-alkanylpyridinium iodides with saturated C_8, C_{10}, C_{12}, and C_{13} alkyl chains showed β values ranging from 0.78 to 0.82, typically.[9]

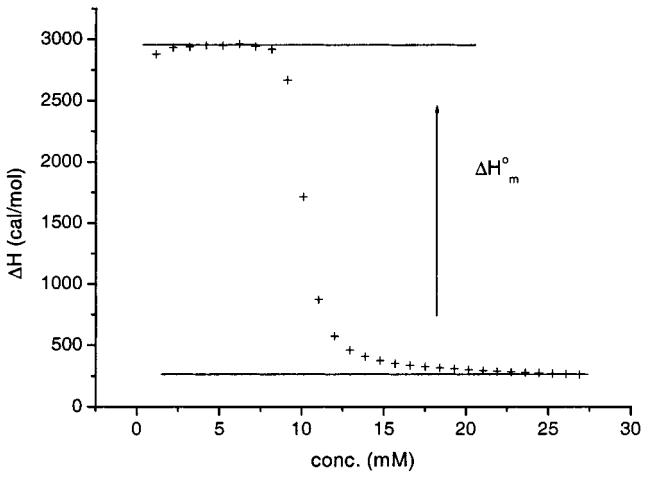

Figure 4. Enthalpy of dilution ($\Delta H°$) of **4** at 25 °C.

Table 2. Thermodynamic Data for Micellization of 1−4 and 6, Determined by Titration Microcalorimetry

surfactant	$\Delta H_m°$ (kJ/mol)	$\Delta G_m°$ (kJ/mol)	$T\Delta S_m°$ (kJ/mol)
1	−12.6	−41.9	29.3
2	−11.6	−37.5	25.9
3	−10.0	−36.9	26.9
4	−11.3	−38.3	27.0
6	−8.70	−39.5	30.8

The change in the cmc as a function of the alkyl chain length of a surfactant can be described by the Shinoda equation[13]

$$\log \text{cmc} = an_c + c \qquad (2)$$

in which n_c represents the number of carbon atoms in a saturated unbranched hydrocarbon chain. For 1-methyl-4-alkylpyridinium iodide surfactants with chain lengths between 8 and 13 carbons, a linear relationship was found.[9] With the use of this equation, the effective chain length for surfactants **2**−**4** and **6** was estimated (Table 1). The insertion of a double bond has the same effect on the cmc as the removal of 0.6−1.2 CH_2 units (Δn) from the corresponding saturated chain.

Thermodynamic Data. To get more insight into the aggregation properties of the surfactants, the thermodynamic data were determined by microcalorimetry. Integration of the areas under the measured signals (microcalorimetry, raw data) yields the dependence of heat of dilution on concentration. In Figure 4, a typical plot is shown.

The difference in enthalpy between the horizontal parts of the s-shaped curve corresponds to $\Delta H_m°$; a cumulative plot yields the cmc.[41] The measured enthalpies of micelle formation ($\Delta H_m°$) are summarized in Table 2. Using the mass action model[42,43] and the measured cmc and β values, the standard Gibbs energy of micelle formation ($\Delta G_m°$) can be estimated from

$$\Delta G_m° = (1 + \beta)RT \ln(\text{cmc}) \qquad (3)$$

where R is the gas constant and T is the absolute

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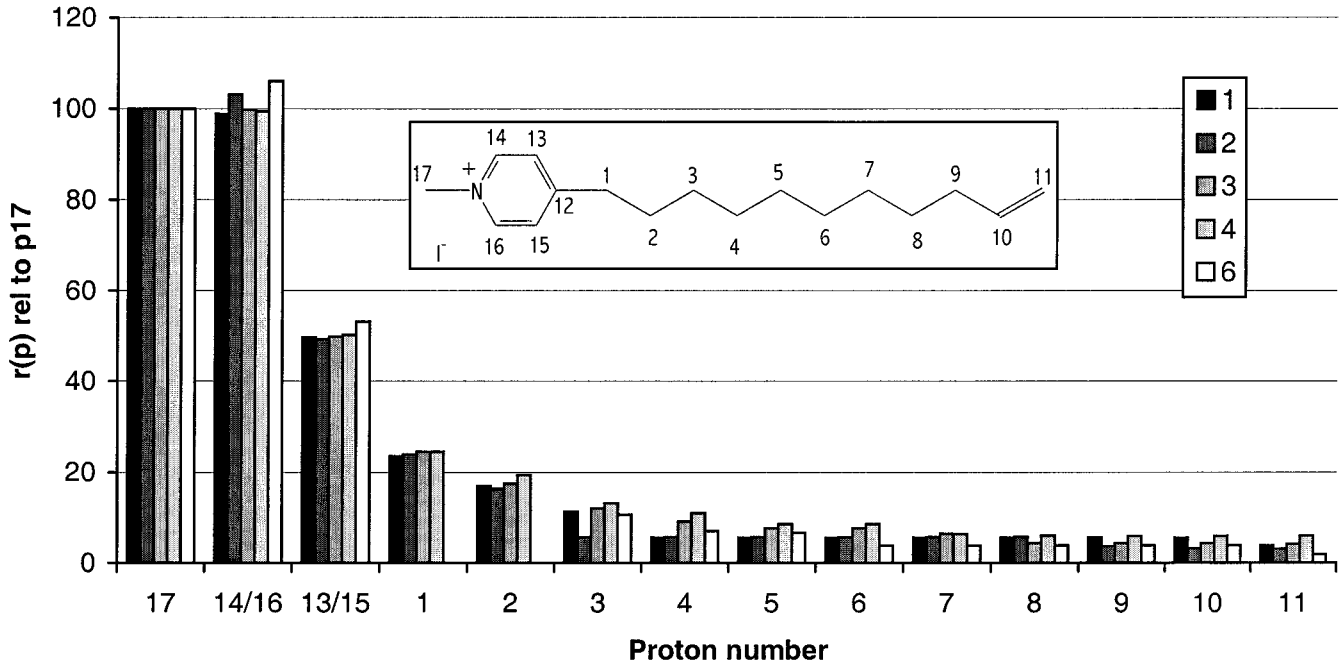

Figure 5. Paramagnetic ion-induced spin−lattice relaxation rates (r_p) of micellar solutions of surfactants **1**−**4** and **6** normalized to the r_p values of the methyl group on the nitrogen. The numbers for the different bars correspond to the surfactant numbers given in Figure 2.

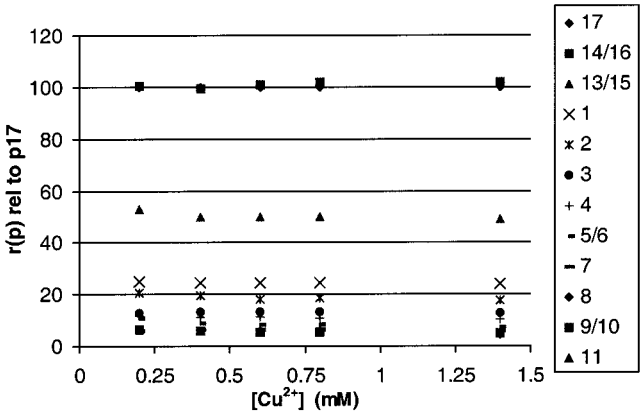

Figure 6. Normalized ratios for surfactant **4** measured at different concentrations of the copper complex. Proton numbers are as given in Figure 5.

temperature. The cmc is expressed in mole fractions units. As discussed by Blandamer et al.,[42] the mass action model is favored above the phase separation model for the relation between the cmc value and the standard Gibbs energy of micelle formation. The entropy of micelle formation ($\Delta S_m°$) can then be calculated using eq 4:

$$T\Delta S_m° = \Delta H_m° - \Delta G_m° \quad (4)$$

The results are summarized in Table 2. The enthalpies of micelle formation are negative; therefore, the process of micelle formation is exothermic. The calculated enthalpies are of the same order as the enthalpies of micelle formation of similar compounds reported earlier.[44] The largest heat effect was measured for surfactant **1**, which also showed the lowest cmc. The surfactants with saturated tails form the most enthalpically favorable aggregates. Bijma et al.[44] found that for an increasing alkyl tail length there is a decreasing enthalpy of micelle formation. Surfactant **6** has the smallest absolute enthalpy of micellization. The entropy of micelle formation, however, is for this surfactant the highest, apparently due to the compensation effect. Surfactants **2** and **4** show almost similar behavior as anticipated on the basis of the comparable cmc values. Because there are only small differences in the thermodynamic data for surfactants **3** and **4** and because the thermodynamic stabilities of the monomers in aqueous solution will be very similar, it can be concluded that the difference in cmc for surfactants **3** and **4** can be attributed to a more hampered packing efficiency of the alkyl chains in the micelles formed from surfactant **3**.

NMR Relaxation Experiments. The experiments described above provide no conclusive insights into the dynamic behavior on a molecular level. NMR T_1 relaxation measurements yield information about the inherent mobility and chemical surroundings of the different nuclei and hence on possible morphological dynamics. Changes in relaxation rates induced by added aliquots of a paramagnetic ion (r_p) can be obtained by subtracting the observed relaxation rates in the absence of these ions from those obtained in the presence of the paramagnetic ion.[19] The exact magnitude of r_p strongly depends on the local concentration of the paramagnetic ion at the micellar surface. In this study, a Cu^{2+}−EDTA complex was added in small aliquots (see Experimental Section). The r_p values were normalized to allow comparison between the different surfactants and are expressed as a percentage of the r_p values of the methyl group at the nitrogen (100% influence of Cu^{2+}). The ^1H spectra did, however, not resolve all the different proton resonances; therefore, several indicative resonances were selected to allow comparison. Figure 5 summarizes the normalized r_p values relative to the surfactant methyl protons for surfactants **1**−**4** and **6**. The carbon numbering is illustrated for surfactant **2**.

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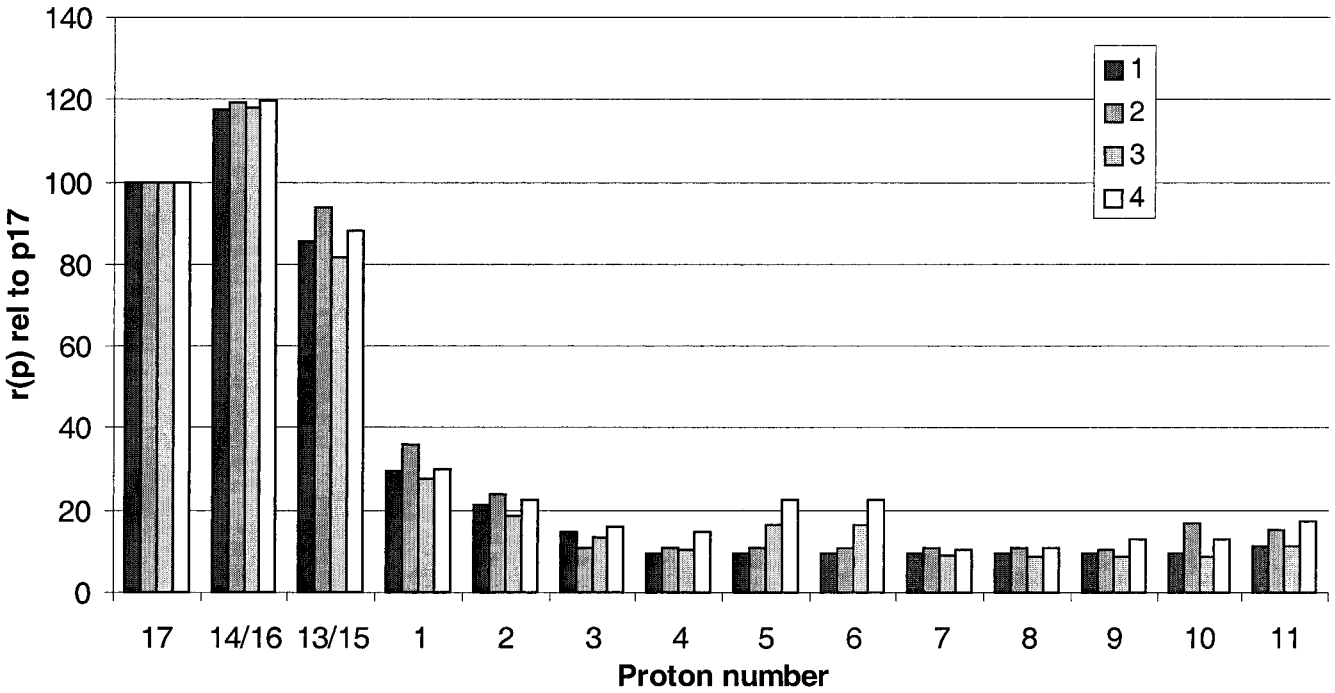

Figure 7. Paramagnetic ion-induced spin−lattice relaxation rates (r_p) of micellar solutions of surfactants **1**−**4** normalized to the r_p values of the methyl group on the nitrogen. Before the r_p values were calculated, the value of **1** was added up to the relaxation times. The numbers for the different bars correspond to the surfactant numbers given in Figure 2.

The data suggest that no large differences in the packing of the micelles for the different surfactants exist. The headgroup protons 17 and 14/16 have similar relative ratios for all the surfactants studied: these protons reside most of the time at the surface of the micelle. For surfactant **4**, the relaxation rates at increasing concentrations of the copper complex were measured in order to determine the influence of the ratio of Cu^{2+}/micelle on the normalized relaxation rates, r_p (Figure 6). It is concluded that the normalized relaxation ratios for the "marker" methyl group (17) and the other resonances are independent on the concentration of the added Cu^{2+} complex. This is consistent with the results obtained by Cabane et al.,[19] who performed similar experiments and concluded that the normalized ratios did not depend on the paramagnetic ion/micelle concentration ratio.

We note that we have made an attempt to avoid potential pitfalls in the comparison of relaxation times just below and above 1 s. Taking the reverse of, for example, relaxation times of 0.6 and 0.8 leads to much larger differences than for a similar manipulation for relaxation times of 1.4 and 1.6. Therefore, a threshold value of 1 was added to all the relaxation times before the actual calculations. These results are summarized in Figure 7.

Interestingly, the results obtained this way show more significant differences in the normalized relaxation times of the respective surfactants. Most significantly, surfactants **3** and **4** show higher normalized relaxation times for the protons 5 and 6 than, for example, surfactant **1** with a saturated tail of the same length. Surfactant **2** shows higher normalized relaxation times for the protons 10 and 11 as compared to the other surfactants. In both cases, these are the protons that are connected to the less hydrophobic part of the tail, the double bond. The results suggest that the protons of a double bond tend to spend more time at the surface of the micelle as compared to the protons at the same positions in a saturated system. Alternatively, the micelles based on surfactants with unsaturated tails might open up the interior of the core to allow water and ions to penetrate more readily and deeply into the core than the saturated equivalents. This clearly induces a larger mobility and more dynamic character of these surfactants.

UV−Vis Experiments. The UV−vis spectra of azo dyes are sensitive to (small) medium effects.[20,45] The maximum absorption band (λ_{max}) for MO is positioned in water at ca. 466 nm and in ethanol at ca. 417 nm, indicating that a more apolar environment leads to a substantial decrease in λ_{max}. It is shown that surfactants also exert a dramatic influence on the absorption spectra.[46] Therefore, the effects of unsaturated alkylpyridinium iodide surfactants on the absorption spectra of MO have been investigated by means of UV−vis spectroscopy. Figure 8 shows the effect of surfactants **1**−**4** and **6** on the absorption spectrum of MO. Surfactant **1** shows the expected effect consistent with that found for other cationic surfactants.[24]

At low concentrations of cationic surfactant, well below the cmc, a new band appears at ca. 385 nm. At surfactant concentrations above the cmc, the maximum absorption band of the dye is positioned at 434 nm, which is common for MO incorporated in a micellar environment. Because the absorption spectrum of MO incorporated in an aqueous solution of 1 mM surfactant shows two maxima (e.g., at 385 and 458 nm; e.g., surfactant **1**), it seems that MO exists as an uncomplexed species in solution and is also part of another type of aggregate, most likely an H-aggregate.[20,24,27] After a few days, small crystals were formed in the solutions at surfactant concentrations below the cmc, which is a common phenomenon.[24] In contrast to previous results,[20,24,27] surfactants **2**−**4** do not show a sharp absorption band at short wavelengths around 385 nm (Figure 8b−d). Surfactant **4** also displays a shoulder around 360 nm; this band can be ascribed to absorption of the surfactant itself. The crystals of the surfactants are

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(46) See, for example: (a) Amire, O. A.; Burrows, H. D. In *Surfactants in Solution*; Mittal, K. L., Bothorel, P., Eds.; Plenum Press: New York, 1986; Vol. 4. (b) Sarkar, M.; Poddar, S. *J. Colloid Interface Sci.* **2000**, *221*, 181.

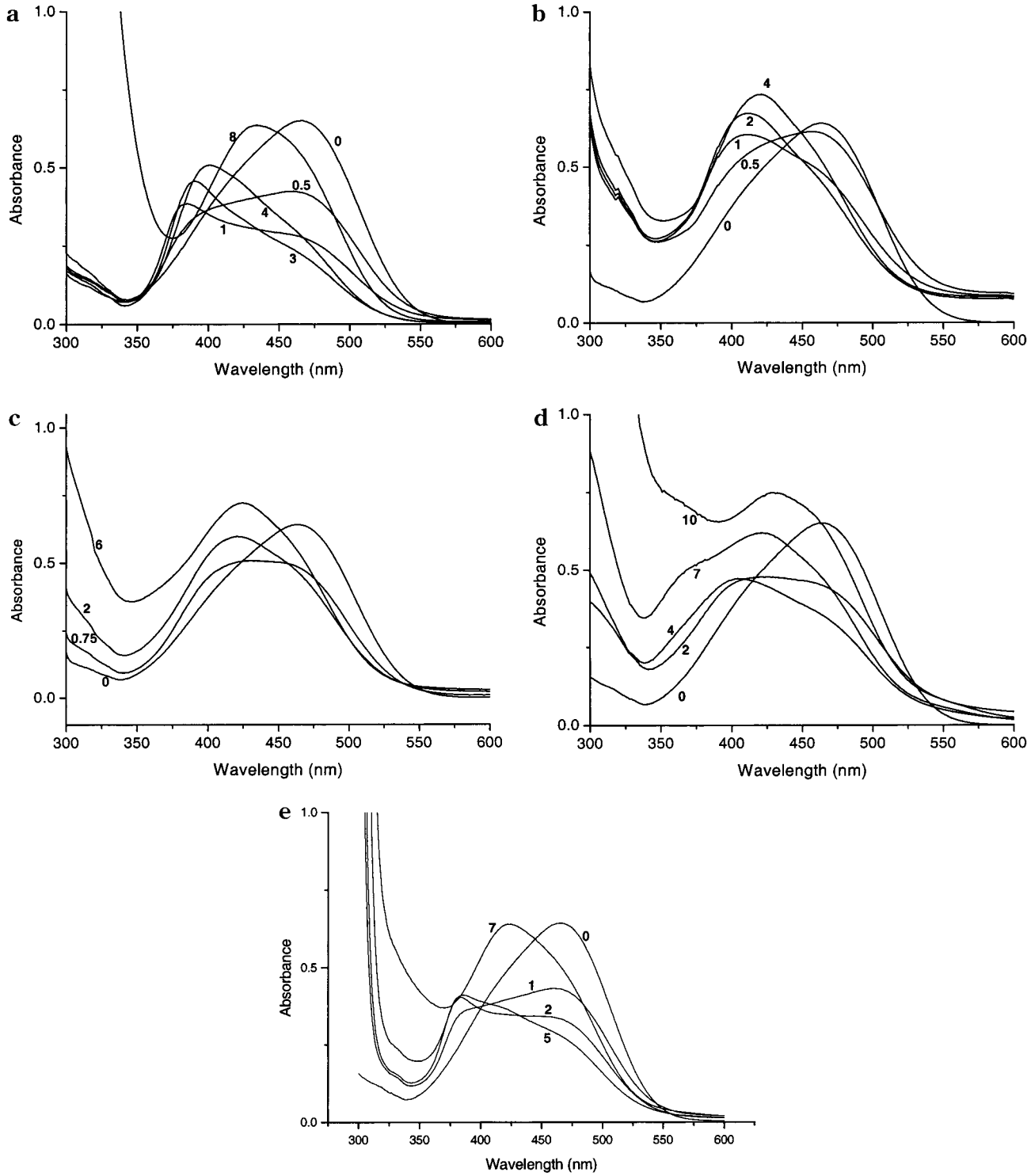

Figure 8. Effect of the surfactants on the absorption spectrum of MO at 25 °C. The numbers represent the concentration of surfactant in millimolar. The concentration of MO was 25 μM. (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **6**.

yellow, most likely due to the formation of a small amount of I_3^-. A UV−vis spectrum of **4** (7.0 mM) in the absence of MO shows a band located at ca. 360 nm. Because a short wavelength absorption band is not observed for MO in aqueous solutions of surfactants **2**−**4**, we conclude that a double bond at the end and in the middle of the alkyl chain hampers the formation of aggregates responsible for the short wavelength absorption band. Strikingly, surfactant **6** did induce a short wavelength absorption band at ca. 383 nm in the spectrum of MO. Interactions of MO and surfactant **5** were also studied. Because of its high Krafft temperature, aggregation could only be studied at low concentrations (≪cmc) of **5**. Surfactant **5** also induced a short wavelength absorption band in the spectrum of MO at concentrations of 1 and 2 mM, typically. Apparently, a double or triple bond adjacent to the headgroup does not hamper the formation of aggregates responsible for the formation of H-aggregates. The increasing absorbance between 300 and 350 nm with an increasing concentration of surfactant (Figure 8) can be ascribed to absorption of the surfactant itself (I_3^- formed from I^-) and/or to an intramolecular charge-transfer absorption band (CT band) of the ionic headgroup.[47] Only above the cmc, the CT band was observed for 1-methyl-

4-dodecylpyridinium iodide at 25 °C.[47] Figure 8a shows a strong increase in absorption between 300 and 375 nm for concentrations above the cmc.

Conclusions

Introduction of unsaturation in the tail of pyridinium iodide surfactants results in an increase of the cmc as compared to the corresponding saturated compounds. Variation of the position and the configuration of the unsaturation leads to different aggregation behavior, as revealed by the cmc values. A double bond at the end of the alkyl chain (**2**) has the same effect as a double bond trans oriented in the middle of the alkyl chain (**4**). A cis double bond in the middle of the alkyl chain (**3**) causes an even higher cmc. The results of NMR T_1 relaxation measurements show that the hydrogens of the double bond tend to be more at the surface of the micelle than the same hydrogens of the saturated compound, indicative for a more loose packing. An unsaturation in the middle and at the end of the alkyl chain has a greater impact on the aggregation behavior than unsaturations near the headgroup (as compared to the saturated compound). This is also suggested by UV−vis experiments of the surfactants in the presence of MO. Surfactants **1**, **5**, and **6** induced the short wavelength absorption band, while surfactants **2**−**4** did not. This effect is most probably due to the hampering of the formation of H-aggregates.

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